SURFACE ANALYSIS OF AN ORIGINAL BRANEMARK IMPLANT FIXTURE AND THREE RELATED CLONES.

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Shortly after the introduction of the Branemark Implant, several manufacturers sold implant components that closely emulated the original Branemark design. Claims of equivalency followed, both directly and indirectly. [1,2] Physically, the replicate products look very similar in overall appearance, size, shape and thread design. Implant surface conditions however, can vary significantly, depending on fixture preparation and handling.[3] It is generally accepted that the outermost atomic layer of the implant surface is a key factor in the osseointegration process. Since the cell - oxide interaction takes place over a few atomic distances, compositional changes occurring at that level can influence the biocompatibility and the osseointegration prognosis of the implant.[4] It cannot therefore be assumed that the clinical results of one implant system will be duplicated by other systems that in appearance, size, shape, and thread design emulate the original fixture.[5] More subtle differences in material, design, surface texture, manufacturing process and method of sterilization, can affect the clinical performance of the implant.[6] An example of this sensitivity was documented by Sennerby et al [7] who reimplanted resterilized screws into a soft tissue bed. The reused screw induced a thicker soft tissue wall and more giant cell activity than the control.

Competing systems must therefore demonstrate equivalency not only on a macroscopic, but a microscopic and, a clinical level as well.

The purpose of this investigation was to compare the surface and near surface composition of representative samples of each clone type with a Branemark Implant. Analysis of the chemical composition of a surface usually involves emission spectroscopy (Table 1). In general, the sample surface is bombarded with a beam of electrons, photons, or ions. As the beam strikes the specimen surface, it initiates a secondary emission, which characterize the elements present.

MATERIALS AND METHODS

Microanalytical surface analysis was performed on a Branemark Implant (Nobelpharma) and three competing clone fixtures. The samples were received from the manufacturer in sealed sterile packaging with the following identification markings:

NOBELPHARMA (NP)	0052-0049-03 exp 11/93
Nobelpharma USA, Inc.	Waltham, MA
SWEDEVENT (SV)	PO9499
Core-Vent Corp.	Encino, CA
OSSEODENT (OD)	#89128
Collagen Biomedical	Palo Alto, CA
IMPLANT INNOVATIONS (II)	23242-5126 steam sterilized
Implant Innovations Inc.	West Palm Beach, FL

The spectroscopic test employed in this investigation were:

1) ENERGY DISPERSIVE X-ray Spectroscopy (EDX)

The implants were analyzed by Kevex Quantum Detector under ultra high vacuum. The implant surface was irradiated with a 10 KeV electron beam. The resulting characteristic X-ray emissions were analyzed by a broad range energy dispersive detector that permitted inclusion of the softer

(low energy) X-rays. The resulting spectra correspond to the chemical elements present within the first 1000 nm of the surface. The sizes of the peaks are related to the concentrations of the elements. The relative sensitivity factors used to calculate atomic concentration from the observed intensities are dependent on the specific architecture of the spectrometer and the prevailing conditions at the time the measurements are made. It is characteristic that all spectrometers change their transmission with time as the spectrometer contaminates and the electron detector degrades. The data obtained and reported was converted to atomic concentration using sensitivity factors determined from thin coatings of $Ti0_2$ on titanium and pyrolitic graphite.

2) AUGER ELECTRON SPECTROSCOPY (AES)

AES provides trace surface analysis at the atomic level with a sensitivity of ~0.1 atomic percent. An electron beam was used to excite the Auger electrons from the top .5 to 2 nm of implant surface. In order to penetrate deeper into the metal, the external surface was slowly eroded in ultrahigh vacuum with an argon ion sputter source. The Auger instrument used was a JEOL Jamp-10S with a cylindrical mirror analyzer. Data was collected in the derivative mode using a 5eV peak -to- peak energy modulation. An electron beam voltage of 10KeV and a beam current of ~0.5 uA was used. The electron beam was defocused to ~10 u to minimize electron beam damage. The ion gun was a differentially pumped Kratos MiniBeam II. It was operated at a voltage of 3 KeV using a current density of ~0.2 mA/cm^2 with argon ions. Actual pressure during sputtering was ~$5x10^{-8}$ Torr. The base pressure before analysis was in the 10^{-10} Torr range. The argon beam removed incremental layers of a predetermined thickness. The resulting

data contains two spectra, one representing the outer surface composition before the argon etch and the other, the surface composition at the ~30 nm level.

3) DEPTH PROFILE

An analysis was also made at ~1 nm increments up to 16.8 nm for the atomic concentration of Ti, S, Fe, C, Si, O, P, and Ca, using the 3 KeV argon ion sputter etch. The sputter yield or rate is dependent on a number of factors such as the material being sputtered, its crystallinity and its orientation to the ion beam. It is well known that metallic oxides sputter at different rates and many sputter more slowly than the pure metal. ALTHOUGH the depth profiles presented in this paper and in the referenced literature assume constant ion sputtering rates, the rate actually increases as the oxide is sputter removed. Absolute sputter rates are unknown because of the continuously changing composition of the specimen with depth. The sputtering rate assumption used in this report is based upon the laboratory standard of a thin film (~300 A^0) of SiO_2 on Si and the arbitrary notion that TiO_2 sputters at 40% of the rate of metallic Ti.

RESULTS AND DISCUSSION

The EDX spectra indicate that all four implant manufacturers use commercially pure titanium stock. The spectrum for the NP sample (fig.1a) contains only the characteristic Ti peaks. The OD EDX (fig.1b) is almost identical to the NP spectra. Both show no detectable contaminants. The SV (fig.1c) and II (fig.1d) spectra both show trace amounts of Si. The Auger survey spectrum for NP (fig.2a) shows Ti, O and small concentrations of S, C and Ca on the surface. After the argon sputter etch, a residual C peak and a small amount of implanted argon residual remain in addition to the Ti and O peaks. Since the ion beam is unidirectional and the specimen surface is not

perfectly smooth, it is difficult to remove 100% of the C.

Metallographically polished pure titanium (99.99 %) was tested under the same conditions as the implant samples to determine if the carbon peaks were the result of contaminants from within the vacuum chamber reacting with the atomically clean Ti ("knock- on" phenomena). The results showed the Ti standard sputtered with a much smaller "knock- on " carbon peak (~10 %) than the implant samples. It is therefore logical to deduce that the resultant carbon peaks are from contaminants within the specimen , possibly machine oil residue. The S and Ca, no longer present after the sputter etch, indicate that they were minor surface contaminants.

The Auger spectrum from the OD sample (fig.2b) contains Ti, O, and small amounts of Si (oxidized form) and S. Both Si and S were quickly sputter etched and were not visible at the 30 nm level. The SiO_2 can also arise from the radio-frequency glow discharge cleaning process if it was improperly applied. Under those circumstances, the quartz glass predictably comes off as a particulate, and not a thin film. The SiO_2 observed in this sample was not particulate and therefore not a result of RFGD.

The SV Auger spectrum (fig.2c) confirms the presence of Si as found in the EDX spectrum and indicates it is in an oxidized form, a residual perhaps of a Si based machining oil or polishing material. Small Cl, F, Ca and Na peaks, possibly residuals of salts from the wash water were also present. The Si and Cl were removed after one sputter cycle indicating these to be only surface contaminants. The Ca, F, and Na however, were still present at the 30 nm level.

The Auger spectrum for the II sample (fig.2d) contained Ca and P (oxidized state) peaks, but not Si. The Si found in the EDX analysis was therefore probably from subsurface material.

Comparative spectra are shown in (fig. 3a,b,c) with the NP spectrum as the baseline. Comparison of the OD (Fig. 3a) and II (Fig. 3b) spectra indicate they closely coincide with NP.
Depth profiles of all four implants showed increasing Ti and decreasing O and C concentration with depth. The C contamination was lowest for the II sample and highest for the NP implant. The NP (fig.4) and OD (fig.5) depth profiles document no other contaminants under the specimen surface. The SV depth profile (fig.6) tracked Ca the full extent of the probe. Salt residues, developed in processing rinse water may be the source of the contaminant. The II sample (fig.7) contained P and Ca throughout most of the 16.8 nm profiled . A probable source for the P may be a phosphoric acid etch used to clean the surface and the Ca may result from the rinse water.

Oxide thickness and surface contaminants are very dependent on manufacturing conditions. To make an implant, C.P. Ti stock is lathed, milled and treated under controlled conditions. The speed and pressure of the instrumentation, surface temperature, exposure to air, the lubricants and coolants used, all influence the nature of the implant surface.[4] Since Ti oxidizes very rapidly, within microseconds a 5 to 10 nm titanium oxide layer is formed.[8] Subsequent manufacturing steps consist of ultrasonic cleaning in a variety of solvents and washes and, steam autoclaving (130-140 C for 20 min). Considerable proprietary secrecy is exercised and the preceding steps generally describe the preparation of the original Branemark fixture. Competing manufacturers have attempted to duplicate and/or enhance surface properties. For example, SV fixtures are acid etched and OD fixtures are treated with radio-frequency glow discharge.[1,9] Evidence suggests that the "cleanest" and most bioactive implant surfaces are obtained following glow discharge treatment.[10,11] In this analysis, the OD sample demonstrated the cleanest oxide surface. Baier and

Meyer[12] point out that inadvertent metal transfer during final tooling can lead to corrosive, erosive and electrolytic surface contaminants that in a biological environment can induce and accelerate deterioration of the implant interface. This is more notable when the fixtures are steam autoclaved. A recent internal quality control audit by NP, indicated that the two fixtures tested had significant amounts of particulate C, Ca, Cl, Si, and smaller amounts of Pb, Sn, Fe, and K present.[13] It was recommended that a metallurgically cleaner surface could more easily be attained if the metal surface was acid etched during the cleaning protocol. This may not be a problem since earlier Auger and EDX analysis, as well as our results, document only minor surface contaminants.[14,15,16] In reviewing ESCA spectral analysis of the oxidized Ti implant surface, Kasemo and Lausmaa [4] noted that there is usually a large C signal, a smaller N signal and traces of Cl, S and Ca present. They attribute the C, N, S, Cl containing molecules to adsorption during preparation procedures. They reported that the Ca usually persisted throughout the oxide layer and may have been the result of surface segregation of minute Ca quantities in the CP Ti stock. Until it is possible to observe and predict how oxide surface alteration and contamination will alter in vivo performance, a high standard of cleanliness and effective decontamination must prevail. [17]

Titanium spontaneously forms a passivating oxide layer of 3 to 15 nm at ambient temperatures when exposed to air or water.[4,8,14,17,18] The predominant oxide is TiO and it is the only oxide stable over the pH range of living tissue. There is no absolute means of measuring TiO thickness. Oxide thickness can be estimated from the depth profiles. McQueen et al [14] arbitrarily established an oxygen concentration of 10 to 20 % as the limit of the oxide layer. Applying the 20% limit to the depth profile data results in the relative oxide thickness reported in Table 2. Another method

described by Lausmaa and Kasemo [19] established the oxide thickness at 50% of the maximum O value at the sample surface. These values are also reported in Table 2.

There is evidence that the oxide continues to grow in vivo. Implants retrieved after 6 and 8 years of function have demonstrated oxide layers of 200 nm.[14] These oxide layers all contained P, Ca, and S in addition to Ti, O, and C. The authors also concluded that TiO as a passivating insulator was essentially "useless" in the long term. Contrary to the expected behavior of decreased growth and eventual cessation, the oxide layer continues as an expanding biologically active entity in living bone. Titanium compounds have been identified in the tissues approximating implant fixtures.[20] Following implant insertion, above normal compound levels have also been documented in rabbit spleen and lung tissue.[21] It is therefore prudent to focus careful attention on any oxide contaminants as these could be leached out in time.

With respect to oxide thickness, it was substantially lower in the RFGD treated fixture. Our data support the results of Wihtol, who compared the effects of RFGD and dry heat sterilization techniques, on oxide layer thickness.[15] Dounddoulakis also observed a thinner oxide layer on RFGD treated samples.[11] At the present time, the significance of the oxide thickness on clinical performance is unknown.

CONCLUSIONS

A "clean" implant surface is a surface with only a native or "thin " oxide present, as demonstrated by metallographically prepared and properly cleaned high purity materials. It is a surface devoid of all impurities and contaminants. Our results indicate that each of the fixtures analyzed demonstrates varying degrees of contamination. Variations in manufacturer production

and cleaning effectiveness were noted. By definition, the OD sample had the cleanest surface and near surface composition. In descending order the next clean surfaces were demonstrated by NP, II and SV. The OD RFGD sample also demonstrated the thinnest oxide layer. As part of the manufacturing protocol, consistent routine surface analysis is advocated to insure the cleanest biologically acceptable surface for implantation. Additional investigation of implant surfaces is necessary to more fully understand all the parameters that influence clinical success.

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Table 1

Spectroscopic Microanalytical Technique

Name	Utility	Technique
EDX - Energy dispersive X-ray analysis	Elemental analysis of the surface to 1000 nm	10 KeV electron beam secondary emissions picked up with X-ray detector,high vacuum

AES,SAM Auger electron spectro scopy /microprobe measured	Elemental analysis .001 to .005 um limit ~.1 atomic %	10 KeV electron beam follows 3 KeV Argon etch.Secondary elect rons (Auger) are quantitatively, ultra high vacuum

TABLE 2

TEST	**CONTAMINANTS**			
	NP	**OD**	**SV**	**II**
EDX	none	none	Si	Si

AUGER (surface)	S,C,Ca	Si(O),S	Si(O),Cl,F, Ca,Na	Ca,P(O)
(30 nm)	C	none	Ca,F,C	C,P,Ca
DEPTH PROFILE	C>	C	C,Ca	C<,P,Ca
* **OXIDE THICKNESS**	17 nm	4 nm	16.5 nm	14 nm
**	10.8 nm	1.8 nm	11.8 nm	10 nm

* Oxide thickness as determined by McQueen et al method. [14]
** Oxide thickness as determined by Lausmaa/Kasemo method. [19]

LEGENDS

Fig.1 Typical EDX spectra showing characteristic Ti peaks. All four spectra indicate commercially pure Ti was used. Nobelpharma (1a) and Osseodent (1b) spectra are almost identical. Both show no detectable contaminants. SwedeVent (1c) and Implant Innovations (1d) spectra show traces of silicone (peak in the 1.9 KeV energy level)

Fig.2 Typical Auger survey illustrating the surface and the 30 nm argon sputter etch spectrum for each of the implant fixtures. The Nobelpharma spectra (2a) shows Ti, O and small

concentrations of S, C, Ca on the surface. After the argon etch, only the C remains, indicating that the S and Ca were minor surface contaminants. The Osseodent spectrum (2b) shows Ti, O, Si, and S peaks on the surface. Both S and Si were easily removed with the argon etch, indicating that they were minor surface contaminants. SwedeVent spectrum (2c) shows Si, Cl, F, Ca, and Na peaks. The Si and Cl were removed with the etch. The Ca, F, and Na however, were still present at the 30 nm depth indicating the contaminants penetrated the oxide surface. Implant Innovations spectra (2d) shows Ca and P(O) peaks at the surface.

Fig.3 Contrasting spectra of the Osseodent (3a), SwedeVent (3b), and Implant Innovation (3c) samples with Nobelpharma as the baseline spectrum. The elements identified are characteristic to the NP spectrum shown in Fig. 2a. The Osseodent (3a) and Implant Innovations (2c) spectra closely coincide with that of the Nobelpharma sample.

Fig.4 Depth profile for the Nobelpharma sample showing Ti, O, and C concentrations. Profile shows no contaminants.

Fig.5 Osseodent depth profile shows Ti, O, and C concentrations. Profile shows no contaminants.

Fig.6 SwedeVent profile shows the characteristic Ti, O, and C concentrations and tracked Ca the full extent of the probe.

Fig.7 Depth profile for Implant Innovations shows the characteristic elements as the sample is penetrated. This sample demonstrated the lowest carbon presence and tracked P and Ca throughout the full extent of the probe. Without the presence of these two contaminants, this profile would have most closely resembled that of Nobelpharma.

ABSTRACT

SELECTED SURFACE CHARACTERISTICS OF SCREW TYPE TITANIUM DENTAL IMPLANT FIXTURES FROM FOUR DIFFERENT MANUFACTURERS WERE EVALUATED. CONSIDERABLE DIFFERENCES IN SURFACE AND NEAR SURFACE CONTAMINANTS WERE DEMONSTRATED. THE RADIO-FREQUENCY GLOW

DISCHARGE (PLASMA) TREATED FIXTURE DEMONSTRATED THE THINNEST TITANIUM OXIDE LAYER. AND THE CLEANEST SURFACE.

KEY WORDS: TITANIUM, DENTAL IMPLANT, SURFACE ANALYSIS, CONTAMINANTS, EMISSION SPECTROSCOPY, OXIDE THICKNESS.